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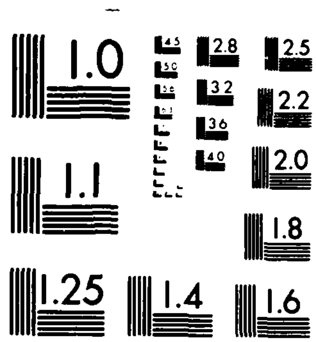


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TECHNICAL REPORT No. 5

# AEROSOL DIRECT FLUORINATION SYNTHESES OF PERFLUOROKETONES

by

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and

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The extension of aerosol direct fluorination techniques to the syntheses of perfluoroketones from their hydrocarbon analogs is described. This continuous flow direct fluorination process is fluorine efficient, causes minimal fragmentation and produces high purity products. The purity of F-3-pentanone, F-3-heptanone, and F-4-heptanone direct from the reactor were 71%, 59% and 92% by weight respectively. Physical losses of feed hydrocarbon, which can be recovered, reduce single pass yields to 13%, 13% and 23% of total feed. Attempted fluorination of cyclopentanone produced

F-pentanoyl fluoride in 61% purity and single pass yield of 24%. No evidence for F-cyclopentanone was found.

REVISED MS #2-354C

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# Aerosol Direct Fluorination-Syntheses of Perfluoroketones

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The aerosol direct fluorination method provides a continuous process for the production of perfluorocarbons from hydrocarbons with efficient fluorine utilization and minimal fragmentation.[1] The application of this process to alkanes, ethers, cyclo alkanes and ketals has been demonstrated.[1] The extension of this novel process to ketones provides direct access to analog perfluoroketones in modest yields, a feat not realized by other direct fluorination methods to any significant degree,[2] although indirect procedures have proven effective for selected cases.[3-8]

Bigelow and Holub, in a comparison of direct (jet) fluorination and the cobalt(III) fluoride (Fowler) process, reported that acetone, methyl ethyl ketone and cyclopentanone could be fluorinated with elemental fluorine to their perfluoro analogs, albeit in poor yields; the cobalt(III) fluoride process, however, cleaved the ketones at a very early stage in the reaction.[2]

Because of the difficulty of producing perfluoroketones directly, numerous indirect methods have been developed.[3-8] For example, the deficiency of the cobalt(III) fluoride process in the production of perfluoroethers can be ameloriated if the ether is already fluorinated on one side.[4] The subsequent sulfuric acid hydrolysis of these halomethyl perfluorocycloalkane ethers (prepared from methanol addition to perfluorocycloalkenes followed by cobalt(III) fluoride fluorination) yielded perfluorocyclopentanone and perfluorocyclohexanone.[4] A similar process, which uses chlorination followed by KF-tetramethylene sulfone metathesis instead of cobalt(III) fluoride fluorination prior to hydrolysis has been reported by Anello, et. al.[5] Another method for the production of perfluoroketones is the decomposition over alumina of the corresponding perfluoroalkylene epoxides prepared from the corresponding cyclic and acyclic alkenes.[6] Perhaps the most useful process on a research scale are the condensation of methyl and ethyl perfluorocarboxylates with sodium,[7] the related reaction of perfluorocarboxylic acids with sodium alkoxide,[8] and the reactions of ethyl perfluoroalkyl carboxylates with perfluoroalkyl grignard or lithium reagents[9] to produce the symmetrical bisperfluoroalkyl ketones and in the latter case potentially the unsymmetrical ketones.

## Results and Discussion

The efficacy of the aerosol process for the direct fluorination of ketones is somewhat surprising. LTG (Low-Temperature-Gradient) Fluorinations have not successfully fluorinated ketones under the usual conditions.[10] The aerosol process is very rich in fluoride ion, thus fluoride catalysed oxidation of the ketone carbonyl group might be expected to produce fluoroxy compounds.[11] It might also be expected that the photochemical finishing stage of the aerosol process would result in photolytic cleavage of the ketone.[12] In reality none of the above problems were manifested in the results. In fact the high concentration of fluoride ion may be beneficial in that the acidity of the medium due to endogeneous hydrogen fluoride is reduced thus minimizing acid catalysed condensation reactions.[13]

In each of the reactions the perfluoroketone was the major product collected. Of the products collected F-3-pentanone, F-3-heptanone and F-4-heptanone were 71%, 59% and 92% of the total by weight; although these numbers are impressive, they obscure a troublesome problem with all of the ketone reactions to date. The aerosol system is dependent on the generation of a particulate aerosol which is ideally crystalline, monodisperse (uniform size) and with little tendency to aggregate. In reality only a few compounds produce near perfect aerosols exhibiting all of the previous properties. Most compounds which produce excellent aerosols are highly symmetrical and pack well in a crystal lattice. Examples are neopentane, adamantane, cycloalkanes, cyclic ethers, and most highly branched, geometrically uniform molecules. Normal alkanes and especially their functional derivatives deviate in varying degrees from this ideal. If the conditions, considered ideal, are met, percent yields based on throughput (amounts injected) and product (collected) percent distributions will differ by only a few percent. As the molecules deviate from this ideal shape, the percent yields based on throughput begin to fall because of physical losses within the aerosol generator and initial reaction stage (see Reference 1). These losses can be significant and result in sometimes significant amounts of unfluorinated or complex mixtures of generally less than trifluorinated products collected at the close of the reactions when the system warms to ambient, or is opened for cleaning between reaction runs.[14] Although significant advances in optimization have been made, this is as much art as science. If no corrections or adjustments are made due to recovered unreacted or partially reacted materials, the yield of F-3-pentanone, F-3-heptanone and F-4-heptanone are 13%, 13% and 23% respectively. It should, however, be emphasized at this point that in virtually all reactions, fragmentation amounts to less than five percent of the total throughput, although in the 3-heptanone fluorination, F-n-butane was isolated in yields approaching that of F-3-heptanone.

Although fragmentation is minimal, occasionally almost total cleavage will occur in a reaction. An example of this is the attempted fluorination of cyclopentanone. The major product collected (61% of the total) was F-pentanoyl fluoride in a yield based on total throughput of 24%. The only other product of significance was F-n-butane (11% of collected product) and numerous very small peaks collectively identified as partly fluorinated acid fluorides from their infrared spectra.

The quantities of materials run were small to achieve more nearly ideal conditions. Throughputs of up to 10 millimoles per hour can be achieved with most compounds on the present reactors of one-half inch cross section, these throughputs usually produce somewhat lower yields and product purity although larger amounts, up to ten grams of fluorocarbons, have been produced this way.

Although considerably more work is necessary, primarily in optimization of aerosol generation before aerosol direct fluorination can be considered a general route to perfluoroketones, clearly the progress so far indicates that this novel direct fluorination process has overcome many obstacles to a direct synthesis of perfluoroketones.

## EXPERIMENTAL

The basic aerosol fluorinator design and a basic description of the process is presented elsewhere.[1] Workup of products following removal of hydrogen fluoride consisted of vacuum line fractionation; infrared assay of fractions; gas chromatographic separation of components using either a 7 meter x 3/8" 13% Fluorosilicone QF-1 (Analabs) stationary phase on 60-80 mesh, acid washed, Chromosorb p conditioned at 225°C (12 hrs) or a 4 meter x 3/8" 10% SE-52 phenyl-methyl silicone rubber on acid washed 60-80 mesh Chromosorb p, conditioned at 250°C (12 hrs). Following gas chromatographic separation (Bendix Model 2300, subambient multi-controller) all products of "significance" were collected, transferred to the vacuum line, assayed and characterized by vapor phase infrared spectrophotometry, PE1330; electron impact (70eV) and chemical ionization ($CH_4$ plasma) mass spectrometry (Hewlett-Packard GC/MS, 5710A GC, 5980 A MS, 5934A Computer); and $^{1}H$ and $^{19}F$ nuclear magnetic resonance (JEOL FX90Q, omniprobe) in $CDCl_3$ with 1% $CFCl_3$ internal standard. The above characterizations (3 pages) are available as Supplementary Material, ordering information is given on any current masthead page. (TR-5 APPENDIX I)

Aerosol Fluorination of 3-Pentanone - Diethyl ketone (Chemical Samples Co.) 99% was used as received. Its vapor pressure at 0°C is such that a flow of 70 cc/min helium through ~50 mL of the material contained in a sparge tube evaporator produces a throughput of 2 millimoles/hr. Details of the aerosol fluorination parameters are given in Table 1. For a four hour, photochemically finished run 0.38g of crude product was separated gas chromatographically on the fluorosilicone QF-1 column (-5°C/2 m; 1°/m to 10°/1 m; 30°/m to 180°/5 m) producing 0.27g of F-3-pentanone (71%, Table 1), a 13% yield based on theoretical throughput. If should be noted that significant quantities of unfluorinated 3-pentanone were found inside the reactor upon warming.

Aerosol Fluorination of 4-Heptanone - Di-n-propyl ketone (Aldrich) was used as received. The vapor pressure at 23°C of 4-heptanone was such that a flow of 165 cc/m of helium through ~50 mL of the material contained in a sparge tube evaporator produces a throughput of 2 millimoles/hr. Details of the aerosol fluorination parameters are given in Table 1. For a four hour, photochemically finished run 0.734g of crude product was separated on the Fluorosilicone QF-1 column (30°/1 m; 2°/m to 60°/1 m; 50°/m to 180°/5 m) producing 0.675g F-4-heptanone (92%) with a yield based on theoretical throughput of 23%. Again unfluorinated 4-heptanone was found in the reactor on warming.

Aerosol Fluorination of Cyclopentanone - Cyclopentanone (Aldri was used as received. The vapor pressure of cyclopentanone at 23°C is that a flow of 112 cc/m helium through 50 mL of the material contained sparge tube evaporator produces a throughput of 2.1 millimoles per hour. Details of the aerosol fluorination parameters are given in Table 1. For a 3 hour, photochemically finished reaction, 0.62g of crude product was separated on the Fluorosilicone QF-1 column (10°/1 m; 1°/m to 30°/1 m; 20°m to 100°/10 m) producing 0.378g of F-pentanoyl fluoride (61%) with a yield based on theoretical throughput of 24%. Cyclopentanone was again found in the reactor on warming.

Aerosol Fluorination of 3-Heptanone - 3-Heptanone (Aldrich) was used as received. Its vapor pressure was too low to get an acceptable throughput by evaporation at room temperature and a modified aerosol generator was adapted to a flash evaporator fed by a syringe pump (SAGE Model 341a) driving a 5.000 mL. Precision Sampling Corp, "Pressure Lok" syringe. A pump speed corresponding to 3.5 millimoles per hour was established and 2.95 mL (2.41g, 21.2 mmole) 3-Heptanone was delivered over a 6 hour period. Details of the aerosol fluorination parameters are given in Table 1. From the crude product (1.65g) was isolated 0.98g (59%) pure _F_-3-heptanone (GLC Temperature Program on the QF-1 column: 25°/2min; 1.5°/min to 60°/1 min.; 50°/min to 180°/20 min.) corresponding to a yield of 13% based on total 3-heptanone injected. Much of the 3-heptanone was recovered unchanged.

Acknowledgement. This work was supported in part by the Office of Naval Research whose support is gratefully acknowledged. Earlier support by the Research Corporation, Cottrell Research Fund is also acknowledged.

TABLE 1

TYPICAL AEROSOL FLUORINATION REACTION PARAMETERS

| Starting Compound | Fluorine Flow mL/m Reactor | Mod. 1 | Mod. 2 | Helium Diluent mL/m Reactor | Mod. 1 | Mod. 2 | Reaction Temp. °C Reactor | Mod. 1 | Mod. 2 | Main Helium Carrier mL/m | Hydrocarbon Throughput millimoles/hr (H.C.carrier) | Overall[a] Stoichiometry hc:$F_2$ | Percent $F_2$ Conc. Final Stage | Reactor Volume mL (α length) | Reaction Time Sec. | Product Distribution % Collected | Product Yield % Theoretical |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3-pentanone | 20 20 | - | - | 20 20 | - | - | -20° | -10° | 10° | 600 | 2.0 (70) | 1:49 | 5.3% | 1355 | 108 | 71% | 13% |
| 4-Heptanone | 20 30 | - | - | 20 20 | - | - | -30° | -20° | 10° | 750 | 2.0 (165) | 1:61 | 5.0% | 1355 | 81 | 92% | 23% |
| 3-Heptanone[c] | - 20 | 20 | 30 | - 150 | 150 | 150 | -40° | -30° | 0° | 500 | 3.5 (500) | 1:56 | 4.6% | (d) | (d) | 59% | 13% |
| Cyclopentanone | 10 15 | 20 | - | 30 30 | 30 | - | -40° | -30° | 10° | 750 | 2.1 (112) | 1:55 | 4.5% | 1355 | 82 | 61% | 24% |

[a] 1 ml./min $F_2$ delivers 2.44 millimoles/hr. $F_2$

[b] F-pentanoyl Fluoride

[c] A flash evaporator hydrocarbon injector fed by syringe pump was used in this reaction.

[d] New Reactor volume not calibrated, similar to previous reactor.

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(1) (a) J. L. Adcock, K. Horita and E. B. Renk, J. Amer. Chem. Soc., 1981, 103, 6937. (b) J. L. Adcock and E. B. Renk, U.S. Patent 4,330,475; May 1982.

(2) F. F. Holub and L. A. Bigelow, J. Amer. Chem. Soc., 1950, 72, 4879.

(3) L. G. Anello and M. Vander Puy, J. Org. Chem., 1982, 47, 377.

(4) A. B. Clayton, R. Stephens and J. C. Tatlow, J. Chem. Soc., 1965, 7370.

(5) L. G. Anello, A. K. Price and R. F. Sweeney, J. Org. Chem., 1968, 33, 2692.

(6) E. P. Moore and A. S. Milian (E. I. duPont de Nemours & Co) U.S. Patent 3,321,515 (1967).

(7) M. Hauptschein and R. A. Braun, J. Amer. Chem. Soc., 1957, 77, 4930.

(8) Douglas W. Wiley (E. I. duPont de Nemours & Co), U.S. Patent 3,091,643, (1963).

(9) O. R. Pierce, E. T. McBee and G. F. Judd, J. Amer. Chem. Soc., 1954, 76, 474; E. T. McBee, C. W. Roberts and S. G. Curtis, J. Amer. Chem. Soc., 1955, 77, 6387.

(10) J. L. Adcock, unpublished results.

(11) O. Ruff, Pitochelli and M. Lustig, J. Amer. Chem. Soc., 1966, 88, 4531 and 1967, 89, 2481; F. A. Hohorst and J. M. Shreeve, Inorg. Synth., 1968, 11, 143.

(12) G. Giacometti, H. Okabe, S. J. Price and E. W. R. Steacie, Can. J. Chem., 1960, 38, 104.

(13) F. A. Carey and R. D. Sundberg, "Advanced Organic Chemistry," Part B, Plenum Press, New York, 1977, p. 34.

(14) In the case of acetone which appears to dissolve the NaF preaerosol particulates, liquid droplets large enough to settle out and collect in the region of the aerosol generator-reactor interface resulted in almost complete recovery of unfluorinated acetone, none of which collected during the reaction but only after warming of the system.

# APPENDIX I

## Supplementary Material

## Characterization of F-Ketones

TABLE 1

CHARACTERIZATION OF F-KETONES
Infrared, Mass Spectra and $^{19}F$ NMR

F-3-Pentanone:

Infrared ($cm^{-1}$): 3620(w), 1780(m), 1320(s), 1230(vs), 1175(vs), 1110(s), 1025(m), 880(m), 830(m), 750(m), 710(s), 600(m).

Mass Spectra [m/e (int.) Formula]:

CI ($CH_4$): 267(100)$C_5F_{10}OH$,M+H; 247(31)$C_5F_9O$, (M-F); 147(31)$C_3F_5O$; 119(14)$C_2F_5$; 69(4)$CF_3$.

EI(70eV):[a] 148(1)$^{13}CC_2F_5O$; 147(40)$C_3F_5O$; 131(1)$C_3F_5$; 128(1)$C_3F_4O$; 119(100)$C_2F_5$; 109(1)$C_3F_3O$; 101(1)$^{13}CCF_4$; 100(12)$C_2F_4$; 98(1)$C_3F_3$; 81(1)$C_2F_3$; 78(1)$C_2F_2O$; 69(32) $CF_3$; 50(2)$CF_2$; 31(3)CF.

$^{19}F$ NMR $\phi_{CFCl_3}$ = 0.0 ppm:

$\phi_{CF_3}$ = -82.03 ppm(s)

J < 1 hz, Integration 3:2

$\phi_{CF_2}$ = -121.38 ppm(s)

F-4-Heptanone:

Infrared ($cm^{-1}$):[b] 1785(m), 1395(m), 1240(s), 1200(m); 1160(m), 1140(m), 1080(m), 1015(m), 845(m), 780(w), 945(m), 925(m), 900(m).

Mass Spectra [m/e (int.) Formula]

CI($CH_4$): 367(39)$C_7F_{14}OH$, M+H; 347(100)$C_7F_{13}O$, M-F.

EI(70eV): 347(7)$C_7F_{13}O$, M-F; 197(15)$C_4F_7O$; 169(100)$C_3F_7$; 119(15)$C_2F_5$; 100(16)$C_2F_4$; 69(81)$CF_3$.

$^{19}F$ NMR $\phi_{CFCl_3}$ = 0.0 ppm:

| | Integral |
|---|---|
| $\phi_{CF_3}$ = -81.16 ppm (m) | 3 |
| $\phi_{CF_2}$ = -126.31 ppm (m) | 2 |
| $\phi_{CF_2}$ = -118.66 ppm (m) | 2 |

(a) See Ref. 11.
(b) A. L. Henne and Wm. C. Francis, J. Amer. Chem. Soc., 1953, 79, 992-4.

TABLE 1 (continued)

F-3-Heptanone:

Infrared ($cm^{-1}$): 1785 (m), 1350(m), 1330(m), 1295(m), 1245(s), 1190(m), 1165 (m), 1140(m), 1110(w), 1050(w), 1020(w), 900(w), 840 (w) 805(w), 745(w), 720(w), 705(w).

Mass Spectra [m/e (int.) Formula]

CI ($CH_4$): 367(86)$C_7F_{14}OH$, ~~M+H~~; 347(97)$C_7F_{13}O$, M-F; 297(5)$C_6F_{11}O$; 247(18)$C_5F_9O$; 219(65)$C_4F_9$; 197(8)$C_4F_7O$; 169(8)$C_3F_7$; 147(28)$C_3F_5O$; 131(28)$C_3F_5$; 119(62)$C_2F_5$; 100(36)$C_2F_4$; 97(12)$C_2F_3O$; 69(100)$CF_3$.

EI (70eV): 219(58)$C_4F_9$; 147(26)$C_3F_5O$; 131(28)$C_3F_5$; 119(100)$C_2F_5$; 100(18)$C_2F_4$; 69(72)$CF_3$.

$^{19}F$ NMR $\phi_{CFCl_3}$ = 0.0 ppm (int) $\underset{a}{CF_3}-\underset{b}{CF_2}-\overset{O}{\overset{\|}{C}}-\underset{c}{CF_2}\underset{d}{CF_2}-\underset{e}{CF_2}-\underset{f}{CF_3}$

$\phi a$ = -81.99 ppm (3)
$\phi b$ = -121.67 (2)

$\phi c$ = -118.01 ppm (2)
$\phi d$ = -124.79 (2)
$\phi e$ = -126.32 (2)
$\phi f$ = -79.82 (3)

coupling are small and multiplets are complex. Assignments comparison to F-3-pentanone and F-4-Heptanone

## TABLE 2

## CHARACTERIZATION OF F-PENTANOYL FLUORIDE

Infrared ($cm^{-1}$): 1880(s), 1350(w), 1275(m), 1265(s), 1240(vs), 1215(s), 1140(s), 1110(s), 1020(s), 945(m), 930(m), 905(m), 875(m), 840(w), 825(w), 815(m), 740(m), 710(m).

Mass Spectra [m/e (int.) Formula]:

CI ($CH_4$): 418 (10.7) $C_{10}F_{14}O_2$; 281 (10.7) $C_5F_9O_3H_2$; 266 (0.7) $C_5F_{10}O$, M; 247 (6.5) $C_5F_9O$, M-F; 220 (4.3) $^{13}CC_3F_9$, 219 (100) $C_4F_9$, M-CFO; 197 (7.2) $C_4F_7O$, M-$CF_3$; 131 (12.5) $C_3F_5$; 103 (5.7) ???; 101 (9.2) $C_2F_4H$; 100 (3.8) $C_2F_4$; 69 (2.7) $CF_3$.

EI (70eV): 219 (3.8) $C_4F_9$; 169 (19) $C_3F_7$; 131 (16.7) $C_3F_5$; 119 (21.6) $C_2F_5$; 100 (10) $C_2F_4$; 78 (5.7) $C_2F_2O$; 69 (100) $CF_3$; 47 (7.3) CFO.

$^{19}F$ NMR[a] $\phi_{CFCl_3} \equiv 0.0$ ppm $\underset{a}{CF_3}-\underset{b}{CF_2}-\underset{c}{CF_2}-\underset{d}{CF_2}-C\overset{O}{\lessgtr}_{F_e}$

(Mult.) [Integ.]

$\phi_a$ = −81.59 ppm (t•t) [3] $J_{ac}$ = 9.76 hz

$J_{ab}$ = 2.14 hz (cont 2.44/1.83 hz)

$\phi_b$ = −126.47 ppm (m) [2]

$J_{bc}$ = 3.05 hz

$\phi_c$ = −123.98 ppm (m) [2]

$J_{bd}$ = 9.76 hz

$J_{ad}$ = 1.83 hz

$\phi_d$ = −118.32 ppm (~q•q) [2]

$J_{ce}+J_{de}$ = 7.33 hz

$\phi_e$ = +24.85 ppm (p) [1]

(a) V. V. Berenblit, V. A. Nikitin, V. P. Sass, L. N. Senyushov, Yu. K. Starobin and Yu. V. Tsyganov, Z. Organicheskoi Khimii, 1979, 15, pp 284-294 (in Translation); J. W. Emsley and L. Phillips, "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. 5, Pergamon Press, Oxford, 1971, p. 123.

# APPENDIX II

# ERRATUM

To Technical Report 4

Erratum to Technical Report 4

Explanation - The characterization of products produced by the Aerosol direct fluorination of tertiary butyl chloride, 2-chloro-2-methylpropane, is not as previously stated to be perfluoro-t-butyl chloride but is in fact perfluoro-isobutyl chloride produced by 1,2-chloride shift and is the sole unfragmented product. The following corrections to the text reflect this reevaluation:

| Page | Line | Delete | Insert |
|---|---|---|---|
| 24 | -2 | F-tert-butyl | F-iso-butyl |
| 25 | 1 | F-t-butyl | F-iso-butyl |
| 35 | -1 | F-tert-butyl | F-iso-butyl |
| 48 | -8 | F-tert-butyl | F-iso-butyl |
| 51 | Insert Replacement Page 51 (Char. Table 10 cont.) | | |
| 57 | 4 | Table II | Table 11 |
| pp 58-62 | Insert Attached Table 11 and renumbered pp 58-60 as 63-65. | | |

TABLE 10 (CONTINUED)

$^{19}F$ NMR: ($\phi_{CFCl_3} \equiv 0$ ppm)  $\underset{a}{CF_3}\underset{b}{CF_2}-\underset{c}{CF_2}-\underset{d}{CF_2Cl}$

$\phi_a$ = -81.7 ppm (t.t)  $J_{ac}$ = 9.89 hz

$J_{ab} \approx J_{ad} \approx$ 1.1 hz

$\phi_b$ = -126.1 ppm (t.m)

$\phi_c$ = -121.6 ppm (q.m)  $J_{cd} \approx$ 1.46 hz

$\phi_d$ = -68.9 ppm (t.q)  $J_{bd}$ = 12.64 hz

F-iso-Butyl Chloride:

Infrared ($cm^{-1}$): 1300(sh), 1280(vs), 1195(s), 1162(s), 1070(w), 1042(m), 988(s), 916(m), 863(s), 751(m), 722(ms).

Mass Spectra [m/e (int.) Formula]:

CI ($CH_4$): 237 (24.2) $C_4F_8{}^{37}Cl$; 235 (77.1) $C_4F_8{}^{35}Cl$; 220 (4.3) $^{13}C^{12}C_3F_9$; 219 (100) $C_4F_9$; 197 (23.8) $C_4F_6{}^{35}Cl$; 131 (5.1) $C_3F_5$; 87 (3.7) $CF_2{}^{37}Cl$; 85 (11.8) $CF_2{}^{35}Cl$.

EI (70eV): 235 (1.3) $C_4F_8{}^{35}Cl$; 219 (37.0) $C_4F_9$; 151 (3.8) $C_3F_6$; 149 (1.3) $C_3F_4{}^{37}Cl$; 147 (4.6) $C_3F_4{}^{35}Cl$; 131 (15.9) $C_3F_5$; 100 (11.6) $C_2F_4$; 87 (21.6) $CF_2{}^{37}Cl$; 85 (68.0) $CF_2{}^{35}Cl$; 69 (100) $CF_3$.

$^{19}F$ NMR: ($\phi_{CFCl_3} \equiv 0$ ppm) [Integ.]  $\underset{a}{(CF_3)_2}\underset{b}{(CF_2Cl)}\underset{c}{CF}$

$\phi_{CF_3}$ = -73.05 ppm (t·d) [14]

$\phi_{CF_2Cl}$ = -61.97 ppm (hept·d) [5]  $J_{ab}$ = 10.74 hz.

$\phi_{CF}$ = -178.53 ppm (hept·t) [3]  $J_{ac} \approx J_{bc}$ = 5.88 hz

Perfluorocyclopentane:

Infrared: Identical with Literature*

Mass Spectra: [m/e (int.) Formula]:

CI ($CH_4$): 131 (100) $C_3F_5$, 121 (16) $C_2H_2F_5$; 103 (14) $C_2H_3F_4$; 100 (21) $C_2F_4$; 81 (69) $C_2F_3$; 69 (29) $CF_3$.

*D. G. Weiblen in "FLUORINE CHEMISTRY," Vol II, Ch. 7, p 471, Fig 3, J. H. Simons, Ed., Academic Press, Inc., New York, N.Y., 1954

TABLE 11

F-Isopentane:

Infrared ($cm^{-1}$):[a] 1260(sh), 1255(vs), 1225(vs), 1147(mw), 1090(w), 1060(vw), 980(m), 930(w), 888(m), 720(m), 635(vw), 610(vw), 525(w).

Mass Spectra [m/e (int.) Formula]:

CI ($CH_4$): 182 (100.0) $C_4F_7H$; 136 (36.5) $C_5F_4$; 132 (51.6) $C_3F_5H$; 69 (50.3) $CF_3$.

EI (70eV): 269 (5.5) $C_5F_{11}$, M-F; 219 (1.6) $C_4F_9$; 200 (2.5) $C_4F_8$; 181 (11.8) $C_4F_7$; 150 (4.5) $C_3F_6$; 131 (21.6) $C_3F_5$; 119 (34.7) $C_2F_5$; 100 (6.6) $C_2F_4$; 69 (100) $CF_3$.

$^{19}F$ NMR ($\phi CFCl_3 \equiv 0.0$ppm, $CDCl_3$):[b] $CF_3-CF_2-CF(CF_3)_2$
a b c d

| | | |
|---|---|---|
| $\phi_a$ = -81.2 ppm (undecet) | [3] $J_{ac}$ = 1.47 | $J_{ab}$ = ?[c] |
| $\phi_d$ = -72.92 ppm (~nonet·d) | [6] $J_{ad}$ = 5.86Hz | $J_{cd}$ = 1.47 Hz |
| $\phi_b$ = -119.9 ppm (heptet·d) | [2] $J_{bd}$ = 10.99 hz | |
| $\phi_c$ = -187.4 ppm (mult) | [1] $J_{bc}$ = 2.93 hz | |

(a) Sadtler, Infrared # 41640P(1967).
(b) R. D. Dresdner, F. N. Thimoe and J. A. Young, J. Amer. Chem. Soc., 1960, 82, 5831.
(c) Some uncertainties exist in coupling constants because 1.47 x 2 = 2.94, 2.93 x 2 = 5.86.

TABLE 11 (CONTINUED)(2)

2-Methyl-3,3-difluorobutane:

Infrared ($cm^{-1}$): 2980(s), 2900(m), 1480(m), 1390(s), 1360(w), 1260(s) 1200(sh,s), 1160(vw), 1110(s), 1050(m), 920(s), 880(w), 730(w).

Mass Spectra [m/e (int.) Formula]:

CI ($CH_4$): 125 (0.6) $C_5H_{10}F_2 \cdot CH_5^+$, 107 (0.7) $C_5H_9F_2$, 89 (100.0) $C_5H_{10}F$, 69 (2.1) $C_5H_9$

EI (70eV): 93 (13.5) $C_4H_7F_2$; 78 (2.0) $C_3H_4F_2$; 77 (7.6) $C_3H_3F_2$; 69 (18.4) $C_5H_9$; 65 (69.7) $C_2F_2H_3$; 47 (8.2) $C_2H_4F$, 43 (100) $C_3H_7$.

$^{19}F$ + $^1H$ NMR[d,e] $\underset{a}{CH_3}-\underset{b}{CF_2}-\underset{c}{CH}(\underset{d}{CH_3})_2$

| | |
|---|---|
| $\delta_a$ = 1.51 ppm (t) | $J_{ab}$ = 18.8 hz |
| $\delta_c$ = 1.5-2.15 ppm(mult) | |
| $\delta_d$ = 1.0 ppm (d) | $J_{cd}$ = 6.83 hz |
| $\phi_b$ = -97.96 ppm (g.d) | $J_{ab}$ = 18.9 hz, $J_{bc}$ = 12.81 hz |

d. $\phi CFCl_3 \equiv 0.0$ppm; 1.0% $CFCl_3$/99% $CDCl_3$; $\delta CHCl_3 \equiv 7.25$ppm.

e. V. I. Golikov, A. M. Aleksandrov, L. A. Alekseeva, and L. M. Yagupol'skii, Zhurnal Organicheskoi Khimii, 1974, 10, 279-99 (In Translation UDC 547.412.22+463.4).

TABLE 11 (CONTINUED)(3)

2-Fluoro-2-Methyl-3,3-difluorobutane:

IR ($cm^{-1}$): 3000(m), 2980(w), 1880(vw), 1485(w), 1390(m), 1260(m), 1170(vs), 1100(w), 1030(w), 940(m), 850(w), 740(w).

Mass Spectra [m/e (int.) Formula]:

CI ($CH_4$): 143 (10.5) $C_5H_9F_3 + CH_5^+$; 125 (17.0) $C_5H_9F_3$; 107 (100) $C_5H_9F_2$; 89 (24.6) $C_5H_{10}F$; 87 (13.7) $C_5H_8F$.

EI (70eV): 111 (3.6) $C_4H_6F_3$, M-$CH_3$; 95 (8.3) $C_4H_9F_2$; 93 (16.2) $C_4H_7F_2$; 69 (15.3) $C_5H_9$ or $CF_3$; 65 (51.9) $C_2H_3F_2$; 61 (100) $C_3H_6F$; 47 (15.6) $C_2H_4F$; 43 (17.5) $C_3H_7$ or $C_2F$; 41 (19.2) $C_3H_5$.

$^{19}F$ and $^1H$ NMR[d] $\underset{a}{CH_3}-\underset{b}{CF_2}-\underset{c}{CF}\underset{d}{(CH_3)_2}$

$\delta_a$ = 1.65 ppm (t·d) $J_{ab}$ = 18.05 hz ($^1H$), $J_{ac}$ = 1.95 hz

$\delta_d$ = 1.737 ppm (d·t) $J_{cd}$ = 21.73 hz ($^1H$), $J_{bc}$ = 1.22 hz

$\delta_b$ = -105.70 ppm (q) $J_{ab}$ = 18.3 hz ($^{19}F$)

$\phi_c$ = -154.21 ppm (heptet) $J_{cd}$ = 21.36 hz ($^{19}F$)

d. $\phi CFCl_3 \equiv 0.0$ppm; 1.0% $CFCl_3$, 99% $CDCl_3$; $\delta CHCl_3 = 7.25$ppm.

TABLE 11 (CONTINUED)(4)

1-Fluoro-2-Methyl-3,3-difluorobutane:

IR ($cm^{-1}$): 2990(m), 2940(sh), 1750(w), 1470(m), 1400(s), 1300(sh,m), 1250(s), 1215(s), 1170(s), 1110(vs), 1040(s), 990(m), 930(s), 870(sh,m), 740(w).

Mass Spectra [m/e (int.) Formula]:

CI ($CH_4$): 143 (12.9) $C_5H_9F_3 + CH_5^+$; 125 (60.4) $C_5H_8F_3$; 123 (19.3) $C_5H_6F_3$; 107 (100) $C_5H_9F_2$; 89 (54.6) $C_5H_{10}F$; 87 (63.1) $C_5H_8F$.

EI (70eV): 93 (10.4) $C_4H_7F_2$; 78 (25.6) $C_3H_4F_2$; 77 (23.2) $C_3H_3F_2$; 69 (86.4) $C_5H_9$; 65 (100) $C_2H_3F_2$; 61 (18.4) $C_3H_6F$.

$^{19}F$ and $^1H$ NMR[d] $\underset{a}{CH_3}-\underset{b}{CF_2}-\underset{c}{CH}(\underset{d}{CH_3})(\underset{e}{CH_2}\underset{f}{F})$

$\delta_a$ = 1.60 ppm (t) $J_{ab}$ = 19.05 hz,

$\delta_c$ = 1.5-2.0 ppm (broad multiplet)

$\delta_d$ = 1.10 ppm (d) $J_{de}$ = 6.83 hz,

$\delta_e$ = 4.5 ppm (d•m) $J_{ef}$ = 47.37 hz ($^1H$)

$\phi_b$ = -95.5 ppm (m)

$\phi_f$ = -226.77 ppm (t•d) $J_{ef}$ = 47.3 hz ($^{19}F$), $J_{cf}$ = 21.37 hz

TABLE 11 (CONTINUED)(5)

2,3-Difluoro-2-methylbutane:

Infrared ($cm^{-1}$): 3000(s), 2950(m), 1465(m), 1385(s), 1170(s), 1120(s), 1085(s), 960(m), 865(m), 740(w).

Mass Spectra [m/e (int.) Formula]:

CI ($CH_4$): 107 (2.1) $C_5H_9F_2$; 89 (100) $C_5H_{10}F$); 69 (9.6) $C_5H_9$; 61 (1.7) $C_3H_6F$.

EI (70eV): 93 (13.0) $C_4H_7F_2$; 79 (25.6) $C_3H_5F_2$; 61 (100) $C_3H_6F$; 60 (17.7) $C_3H_5F$; 47 (14.4) $C_2H_4F$.

$^{19}F$ and $^{1}H$ NMR[d,e] $\underset{a}{CH_3}\underset{bc}{CHF}\underset{d}{CF}\underset{e}{(CH_3)_2}$

| | |
|---|---|
| $\delta_a$ = 1.32 (d•d•d) | $J_{ab}$ = 6.6 hz |
| $\delta_b$ = 4.47 (d•q•d) | $J_{ac}$ = 23.2 hz |
| $\delta_e$ = 1.34 (d•d) | $J_{ad}$ ≈ 1.0 hz |
| $\phi_c$ = -151.60 (d•d•hept.) | $J_{bc}$ = 47.6 hz |
| $\phi_d$ = -184.32 (m•d•q•d) | $J_{bd}$ = 12.7 hz |
| | $J_{cd}$ = 9.8 hz |
| | $J_{ce}$ = 2.0 hz |
| | $J_{de}$ = 21.5 hz |

d. $\phi_{CFCl_3} \equiv 0.0$ ppm; 1.0% $CFCl_3$/99% $CDCl_3$; $\delta CHCl_3 \equiv 7.25$ ppm.

e. W. J. Middleton, J. Org. Chem., 1975, 40, 574-8; $\phi_c = -152.0$ and $\phi_d = -185.5$ ppm.

# APPENDIX III

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